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61,366/60

~~1740~~ PATENT SPECIFICATION

Complete Specification Lodged 9th June, 1960.

Application Lodged (No. 61,366/60) 9th June, 1960.

Applicant Pechiney Compagnie De Produits Chimiques Et Electrometallurgiques.

Actual Inventors .. Jacques Coursier and Michel Moutach.

Convention Application.

(France 13th June, 1959 No. 797424 and 22nd April, 1960 No. 825027)

LAPSED BEFORE ACCEPTANCE.

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COMPLETE SPECIFICATION.

PROCESS FOR THE PRODUCTION OF PURE METAL.

The following statement is a full description of this invention, including the best method of performing it known to us:-

The present invention which results from the researches of M. Jacques Coursier and M. Michel Moutach concerns the preparation of niobium and/or tantalum by carbothermal reduction of their oxides and is related, more particularly, to the production of pure niobium, pure tantalum and/or pure alloys of tantalum and niobium.

It is known, on the one hand, that it is possible to commercially obtain more or less pure niobium or tantalum by various processes and, for instance: by reduction of pure niobium or tantalum hemipentoxide with a reducing metal, such as, for example, aluminium, calcium, magnesium; by reduction of pure niobium or tantalum pentachloride with hydrogen; by reduction of tantalum and potassium or niobium and potassium double fluoride with sodium; or also by fusion electrolysis of potassium fluotantalate or fluoniobate.

These various processes present more or less severe drawbacks and, quite especially, they very seldom enable a pure and ductile metal to be obtained, avoiding the preparation of intermediate compounds is rather difficult, and/or the processes are expensive.

It is known, on the other hand, to prepare niobium or tantalum by carbothermal reduction of their oxides, such reduction being accomplished in several steps. In a first step, a stoichiometric mixture of carbon and niobium or tantalum oxide is first heated

to 1650 - 1700°C. and a non ductile mixture containing about 95% metal, with high oxygen and carbon contents, is obtained; this mixture is then crushed and after its $\frac{C}{O}$ ratio has been

corrected, is heated for several hours at a temperature of the order of 1700-2000°C, thus producing a new, equally non ductile mixture containing about 98% metal and with still higher oxygen and carbon contents. This mixture is hydrogenated, crushed and heated under a vacuum for several hours at a temperature range between 1800 and 2100°C after a little pentoxide of said metal has been added to it; and now a comparatively pure, ductile metal is obtained containing of the order of 0.05 to 0.10 % carbon and about 500 ppm oxygen. Such a process is described, for instance, in the paper of M. F. Joly at the second International Conference of the United Nations on the peaceful utilization of atomic energy (Geneva 1958) A/CONF. 15/P/1274 - Nuclear Science Abstr. No. 8 (suppl.) 30/4/1959 - p. 908.

The present invention has for its object a process for the production of pure tantalum, pure niobium and pure tantalum-niobium alloys containing directly less than 0.15% carbon by weight and less than 0.8% oxygen by weight and, preferably, of the order of 100 to 700 ppm carbon and of the order of 500 to 1000 ppm oxygen.

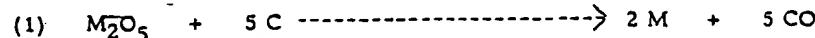
The invention has also for its object a process for the production of ductile tantalum, niobium and tantalum-niobium alloys exhibiting a Vickers hardness at the utmost equal or even less than 80.

Moreover the invention has for its object a process for the production of immediately melting niobium, tantalum and niobium-tantalum alloys, without it being necessary to previously subject them to a sintering operation.

The other objects of the invention will be disclosed in the course of the following description.

The process which is the object of the present invention comprises the following steps:

- mixing a powder substantially consisting of niobium and/or tantalum hemipentoxide, the grain size of which is at the utmost equal to 0.8 millimeter, with another powder substantially consisting of carbon the grain size of which is at the utmost equal to 0.8 millimeter, the amount of oxide thus put into contact with the carbon being more than that corresponding to the stoichiometric ratio in the following reduction reaction:



in which M represents tantalum and/or niobium;

- heating the thus obtained mixture to temperatures between about 2000°C and about 2500°C in order that the above defined reaction may occur.

The applicant has effectively established that in order to directly obtain pure niobium, pure tantalum or pure tantalum-niobium alloys by carbothermal reduction, it was absolutely necessary, firstly, that the metallic oxide molar ratio of the elements brought to carbon

react with one another be higher than the stoichiometric ratio according to the equation (1), which is 0.200, and preferably lies between 0.201 and 0.210 and, secondly, that the metallic oxide and the carbon be previously prepared in very fine form, the grain size of oxide and carbon being at the utmost equal to 0.8 mm and, preferably, lying between about 0.3 mm and 0.08 mm.

This is precisely stated in the two following tables. Table I shows the effect of granulometry on the carbon content of the obtained metal, carbon being the most objectionable impurity. Table II shows the effect of the M_2O_5 molar ratio on the residual carbon

and metallic oxide content in the obtained metal; moreover, let us point out, on this ground, that there is a rapid increase in the oxygen content when this molar ratio becomes lower than the stoichiometric ratio.

TABLE I

Grain size (mm)	1.21-0.8	0.8-0.31	0.31-0.16	0.16-0.08	< 0.08
C (%)	0.3	0.15	0.36	0.05	0.065

TABLE II

M_2O_5	0.200	0.201	0.204	0.210
C				
C (ppm)	> 3000	about 400 - 800	about 150 - 300	about 400 - 800
O_2 (%)	> 0.1	about 0.05 - 0.1	about 0.05 - 0.1	about 0.5 - 1.0

The carbon used may have any origin and, without this listing being considered limiting, it may be charcoal, petroleum coke, either raw or calcined, chemically purified coals, coked and calcined carbohydrates, carbon obtained by thermal cracking of for instance petroleum type hydrocarbons, possibly in the very contact with oxide particles, etc... According to a special embodiment of the present invention, use is made of carbon black, containing no ashes, which has been previously calcined under vacuum at a temperature higher than $1300^{\circ}C$ and preferably of the order of about $2100^{\circ}C$.

Besides, use is made of practically pure metallic hemipentoxide and its purity rate is, preferably, higher than 99% and of the order of 99.5%.

The intimate putting into contact of tantalum oxide and carbon is carried out by any known mixing procedure and, for example, by agitation, kneading, crushing, agglomeration, etc...

According to a preferred though non limiting embodiment of the present invention, the mixture obtained after uniform kneading, for instance, is agglomerated later on,

for example in the form of pellets, obtained by compression. Thus, the applicant has found that interesting results are obtained more particularly when using pellets with a ratio of height to diameter less than 1 and of the order of 0.5, which, though being non limiting, also constitutes an object of the invention.

Besides, the applicant has established that the reduction reaction according to the above mentioned reaction (1) is achieved by heating, preferably under a vacuum, less than one milliliter mercury and, for instance, of the order of a few tens of microns, at a temperature between about 2000°C and about 2500°C and, preferably, of the order of $2150 \pm 50^{\circ}\text{C}$ or so for niobium and of the order of $2350 \pm 50^{\circ}\text{C}$ or so for tantalum, in a crucible substantially consisting of carbon, more precisely graphite. The crucible is previously internally covered with a thin layer, substantially consisting of tantalum and/or niobium, and/or tantalum and/or niobium carbide, the thickness of which is less than 1 mm and, in preference, of the order of 0.5 mm or so; this constitutes another object of the invention.

According to a preferred though non limiting embodiment of the invention, such layer substantially consisting of metallic carbide and metal is obtained by carbothermal reduction of niobium and/or tantalum oxide by heating to a temperature higher than 2000°C and, preferably, of the order of 2300°C , a layer substantially consisting of niobium and/or tantalum hemipentoxide with a portion of the carbon which forms the crucible. Thus, for example, such a coating is carried out in the following way: the internal wall of the graphite crucible is coated with a layer of niobium and/or tantalum hemipentoxide, of the order of one millimeter thickness; then the crucible is heated to about 2300°C so that the graphite in the crucible reacts with the oxide giving rise to a layer substantially consisting of metallic carbide and metal.

The pure metal obtained according to the present invention is eventually reduced to a powder, then sintered by heating under a vacuum. In order to facilitate this crushing of the metal, said metal is first converted to its much more brittle hydride. The applicant has established that this hydridation may be achieved directly in the production furnace; thus, according to a preferred embodiment of the invention, in the furnace wherein the carbothermal reduction treatment which is the object of the present invention has previously been carried out, hydrogen is injected in the course of the cooling step of the thus obtained metal when the temperature is less than 800°C and, preferably, of the order of 650°C . this also constitutes an object of the present invention.

The metallic hydride is then finely comminuted, sieved through sieve 400 with mesh voids of 37.5 microns, degassed by heating at 1000°C microns under a vacuum, then sintered and last occasionally cold rolled into sheets of different thicknesses.

The following examples which in no way may be considered limiting aim only at illustrating the various objects of the present process.

EXAMPLE 1. By uniform mixing, a thorough mixture is made of :

- 522.35 g "Carbon black", previously calcined for 1/2 hour at 2100°C under a vacuum, then crushed and sieved through sieve 200 (0.08 mm mesh voids), and
- 4121 g tantalum hemipentoxide, previously sieved through sieve 55 (0.31 mm mesh voids) and having the following impurities as determined on spectrographical analysis:

Al.....	0.01%	:	Nb.....	0.1
Cu	0.005%	:	Na	traces

Si	0.01-0.02%	: Sn	traces
Fe	0.01-0.02%	: Mn	light traces
Ti	non visible	: C	0.009-0.01%

The thorough mixture thus obtained is now divided into practically equal portions which, afterwards, are pressed in order to product pellets the density of which is nearly 2.2 and of 88 mm diameter and 35 mm thickness.

These pellets are placed in a graphite crucible, previously internally coated, as has been said above, with a layer about 0.5 mm thick substantially consisting of tantalum carbide and metallic tantalum, the same coating being given to the graphite cover to be put on top of the crucible. Crucible and cover have equally been previously drilled with holes.

The crucible which contains said pellets is covered with its cover, then placed in the heating zone of the resistor of the electric furnace. Then the furnace is evacuated and when a vacuum of the order of 30 microns has been obtained, the furnace is progressively heated until reaching, within about 75 minutes, a temperature neighbouring 2300°C which is maintained therein later on for about 150 minutes. Then heating is stopped and the furnace allowed to cool.

After about twenty minutes, when the temperature is of the order of 650 to 700°C, hydrogen is then injected into the furnace and a slight hydrogen overpressure is maintained therein for about one hour.

About 3120 g tantalum hydride are then recovered and are crushed and sieved through sieve 400 (37.5 microns mesh voids). Afterwards this powder is washed with aqua regia so as to remove iron, which has been introduced during crushing, then dried and decomposed under a vacuum, on heating at about 1000°C.

In this way, pure tantalum, containing about 0.025% of carbon is obtained; its increase in weight on being calcined at 900°C in the presence of oxygen is about 21.9% while theoretically that of tantalum, initially perfectly deprived of oxygen, would be 22.11%.

This pure metal is ductile and its Vickers hardness is about 65.

EXAMPLE 2. In the same way as according to example 1, pellets are prepared from:

— 442 g. carbon black, previously calcined for 1/2 hour under a vacuum, crushed and sieved through sieve 400, and

— 2000 g niobium hemipentoxide, previously sieved through sieve 55, and having the following composition:

Nb ₂ O ₅	99.5%	: Fe ₂ O ₃	0.01-0.02%
Ta ₂ O ₅	non dosable	: P ₂ O ₅	traces
SiO ₂	0.1-0.3%	: Na ₂ O	about 0.02%
TiO ₂	0.015-0.04%	: heavy metals	traces

Thus pellets are obtained with a density in the neighbourhood of 1.3.

The crucible, internally coated with a layer 0.5 mm thick substantially consisting of niobium carbide and metallic niobium, and which contains said pellets, is heated within 95 minutes under a vacuum of the order of 40 microns, at a temperature neighbouring 2150°C at which it is maintained for about 75 minutes.

Then the furnace is cooled under a vacuum for about 2 hours and then a block of 1400 g niobium is obtained, the carbon content of which is 0.02% and that of oxygen about 0.2%, which may be pressed, then melted under a vacuum in an arc furnace with a consumable electrode.

EXAMPLE 3. Thorough mixing is made of:

- a mixture substantially consisting of 45.82 parts niobium hemipentoxide by weight and 39.11 parts tantalum hemipentoxide by weight, sieved through sieve 200, and
- 15.07 parts carbon black by weight, previously calcined at 2100°C, sieved through sieve 55.

The thus obtained mixture is pelleted later on, as has been described in example 1 or 2, and the pellets are placed in a graphite crucible the internal wall of which has been coated beforehand with a layer about 0.5 mm thick consisting of niobium and/or tantalum carbide and niobium and/or tantalum.

Then, this crucible is heated within about 60 minutes under a vacuum of 30 to 40 microns to about 2300 - 2350°C and is maintained at this temperature for about 45 minutes.

After cooling, a niobium-tantalum metallic alloy is obtained with a ratio between both constituents by weight practically equal to 1, and containing of the order of 0.1% oxygen and 0.003% carbon.

The claims defining the invention are as follows:

1. Process for the production of pure metal of the group consisting of niobium, tantalum and their alloys, containing less than 0.15% carbon by weight and less than 0.8% oxygen by carbothermal reduction, at high temperature, of their oxides, wherein:
 - a powder, substantially consisting of said metal hemipentoxide, having a grain size at the utmost equal to 0.8 mm, is mixed with another powder, substantially consisting of carbon, having a grain size at the utmost equal to 0.8 mm, the hemipentoxide molar ratio being more carbon than the stoichiometric ratio corresponding to the reaction:



- and then the obtained mixture is heated to temperatures between about 2000°C and about 2500°C. (13th June, 1959).

2. Process according to claim 1 wherein the M₂O₅ ratio is comprised between 0.201 and 0.210. (22nd April, 1960).

3. Process according to claims 1 or 2 wherein the grain size of the oxide grains is between about 0.71 mm and about 0.08 mm. (22nd April, 1960).

4. Process according to any one of claims 1 to 3 wherein the grain size

of the carbon grains is between about 0.31 mm and about 0.08 mm. (22nd April, 1960).

5. Process according to any one of the preceding claims wherein a mixture of niobium oxide and carbon is heated under a vacuum at about 2150°C. (13th June, 1959).

6. Process according to any one of claims 1 to 4 wherein a mixture of tantalum oxide and carbon is heated under a vacuum at about 2350°C. (22nd April, 1960).

7. Process according to any one of the preceding claims wherein said carbon substantially consists of carbon black, containing no ashes, which has been previously calcined under a vacuum at temperature superior to 1300°C and, preferably, of the order of 2100°C. (13th June, 1959).

8. Process according to any one of the preceding claims wherein the obtained metal is put into contact with hydrogen in the course of its cooling down to temperature lower than 800°C and, preferably, of the order of 650°C, so that the metallic hydride is produced directly in the same furnace. (13th June, 1959).

9. Process according to any one of the preceding claims, wherein said mixture is heated in a graphite crucible, internally coated with a layer substantially consisting of the carbide of said metal and of said metal. (13th June, 1959).

10. Process according to claim 9 wherein said layer is previously produced by reduction of an oxide layer of said metal with the carbon of said crucible, on heating to temperature higher than 2000°C and, preferably, of the order of 2300°C. (13th June, 1959).

SPRUSON & FERGUSON.
Patent Attorneys for Applicant.

Related Art:

<u>Serial No.</u>	<u>Application No.</u>	<u>Classification.</u>
103, 104	4332/26 2069/37	15.2; 14.2 15.2; 15.4; 08.5.

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